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ARTICLE

Size of the Dynamic Bead in Polymers

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ABSTRACT: Presented analysis of neutron, mechanical, and MD simulation data available in the literature demonstrates that the dynamic bead size (the smallest subchain that still exhibits the Rouse-like dynamics) in most of the polymers is significantly larger than the traditionally defined Kuhn segment. Moreover, our analysis emphasizes that even the static bead size (e.g., chain statistics) disagrees with the Kuhn segment length. We demonstrate that the deficiency of the Kuhn segment definition is based on the assumption of a chain being completely extended inside a single bead. The analysis suggests that representation of a real polymer chain by the bead-and-spring model with a single parameter C_∞ cannot be correct. One needs more parameters to reflect correctly details of the chain structure in the bead-and-spring model.

I. Introduction

Traditional physical models of polymers are based on simplified presentation of a long macromolecule by a bead-and-spring chain. This simple model of the freely jointed chain provides a clear description of the chain statistics and is used in many models, including Rouse and reptation models.[1−3] In particular, it relates the averaged end-to-end distance of the chain R_{EE} to the number N and the length b of the links (springs): $\langle R_{EE}^2\rangle = Nb^2$. To match any real polymeric chain to the bead-and-spring model, a few parameters are introduced that hide the chemical differences of the real macromolecules. One of them is the characteristic ratio C_∞ that connects R_{EE} of the real chain to the number of its backbone links n and their length l_0:[1−3]

$$\langle R_{EE}^2\rangle = C_\infty n l_0^2 \tag{1}$$

Another broadly used parameter is the Kuhn segment length l_K that connects the length of the bead-and-spring link to parameters of the real chain. It is traditionally[1−4] defined as $l_K \approx C_\infty l_0$. The bead and spring model provides a possibility to replace the real chemical structure of the molecule, its various conformational states, and their energies by a few parameters.

The Kuhn segment is introduced not only to describe the statistics and structure of a linear polymer chain but also to describe its dynamics and rheological properties. In that case the so-called dynamic bead size (the smallest Rouse subchain) is associated with the same Kuhn segment. For decades the Rouse model has been tested using mostly rheological studies. However, mechanical experiments do not provide any direct measure of the dynamic bead size. Developments in neutron scattering spectroscopy open possibilities to measure dynamics at different length scales. As a result, direct estimates of the length of the dynamic bead size become possible. Already early neutron scattering measurements[5] revealed a strong disagreement between the Kuhn segment and the experimentally estimated dynamic bead size. Although this problem was raised almost 30 years ago, it did not receive sufficient attention and remains one of the "unsolved mysteries of polymer viscoelasticity".[6] It affects our understanding of polymer dynamics on a shorter time scales and overall polymer behavior on the nanometer length scale.

This paper presents an overview of neutron scattering studies of chain dynamics in various polymers. Our analysis emphasizes a significant difference between traditionally defined Kuhn segment and the dynamic bead size estimated from neutron scattering for many polymers, some in solutions and many in polymer melts. With the exception of poly(dimethylsiloxane) (PDMS) and poly(ethylene oxide) (PEO), the dynamic bead size appears to be significantly larger than l_K. In addition, we present literature data based on MD simulations and mechanical measurements that also emphasize the problem of the Rouse model at lower molecular weights. Moreover, our analysis demonstrates that even the static bead size is inconsistent with the length of the traditionally defined Kuhn segment. The final part of the presented analysis demonstrates the deficiency of the traditional definition of the Kuhn segment.

II. Neutron Scattering Studies of the Rouse Dynamics

Neutrons scatter on the nucleus and in this way provide a direct probe of atomic motions. As all other scattering techniques, neutron scattering provides not only the characteristic time scale of molecular motions but also their length scale and geometry through variations of the scattering wavevector Q. The neutron spin−echo (NSE) technique covers a broad enough time range to study chain dynamics at high temperatures. It measures the intermediate scattering function $S(Q,t)$. The Rouse model provides a clear prediction for the behavior of $S(Q,t)$.[7−10] In particular, the decay rate should follow Q^4 dependence[7−10] (and Q^3 in the case of Zimm dynamics in a solution). Richter and co-workers demonstrated that Rouse dynamics indeed can describe the NSE data well for many polymers and a good overview of the NSE data is presented in ref 10. The behavior of the $S(Q,t)$, however, starts to deviate from the expected Rouse behavior at higher Q. This deviation indicates the length scale below which pure Rouse dynamics ceases to exist and other contributions (e.g., segmental and sub-Rouse dynamics[10−12]) appear.

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Table 1. Length of Traditionally Defined Kuhn Segment and Dynamic Bead Size Estimated Using Neutron Scattering Spectroscopy[a]

polymer		$10^3 M_n$, g/mol	C_∞	l_K, Å	Q_x, Å^{-1}	b, Å	E^*, kcal/mol	T, K	E^*/kT
polyisoprene[10] (PI)		81	4.6	8.2	0.2	31	3.1[b]	330	4.7
poly(vinylethylene)[10] (PVE)		82	6.6	15	0.15	42	3.3[c]	330	5.0
polyisobutylene[15] (PIB)		3.7	6.7	14	0.15	42	5.7[d]	417	6.9
poly(ethylene oxide)[16] (PEO)		24	6.7	11	0.6	11	1.4[e]	350	2.0
poly(dimethylsiloxane)[5,15] (PDMS)	melt	5.9	6.8	13	0.4	16	< 0.6[f]	373	< 0.8
	solution	15						303	< 1.0
polyethylene[17] (PE)		1.6	7.4	14	0.14	45	2.9[g]	509	2.9
polystyrene[5] (PS) (solution)		55	9.5	18	0.114	55	3[h]	303	5.0

[a] Data for C_∞ and l_K are taken from refs 13 and 14. The dynamic bead size b is estimated as $\sim 2\pi/Q_x$. Rotational energy barriers are compared to kT in corresponding NSE experiment. [b] Reference 18 and 19. [c] Reference 20. [d] References 21 and 22. [e] References 22, 23, and 24. [f] References 25 and 26. [g] References 21 and 27. [h] References 22 and 28.

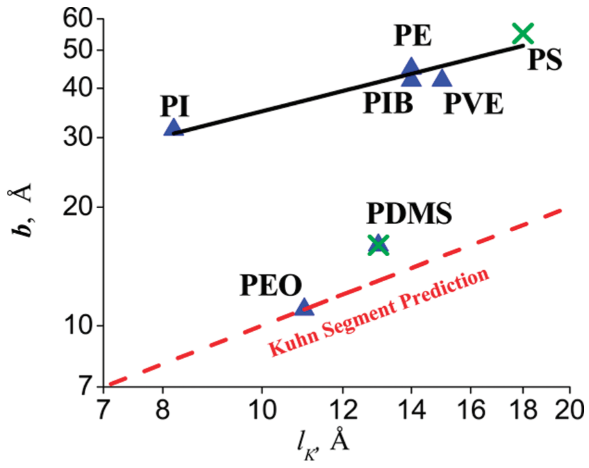

Figure 1. Dynamic bead size b in polymer melts (▲) and in Θ-solutions (×) versus the Kuhn segment length, l_K. The dashed line represents the expected value for the dynamic bead size being equal to the Kuhn segment length. The solid line represents the linear fit to the neutron scattering data for all the polymers, except PDMS and PEO.

The first attempt to estimate the dynamic bead size (the smallest Rouse/Zimm subchain) from the Q dependence of the NSE decay rate has been done in a Θ-solution by Higgins and co-workers.[5] Their analysis revealed a surprising result: although the bead size in PDMS, $b \sim 16$ Å, appears to be close to the expected length of the Kuhn segment, the estimated dynamic bead size in polystyrene (PS), $b \sim 55$ Å, came out to be ~2.5 times larger than l_K.[13] This surprising result has been emphasized in the work by Higgins et al.[5] but was never explained and did not get enough attention.

Later developments of NSE technique provided a possibility to study chain dynamics in polymer melts. Detailed analysis of the Q dependence of the decay rate indeed reveals the expected Q^4 dependence. This dependence, however, exists only up to a particular wavevector[10] Q_x and then changes to a different behavior at higher Q. The value of Q_x depends on the polymer studied and indicates the smallest length scale in polymer dynamics where the Rouse behavior is still valid. These studies allow direct estimate of the smallest Rouse subchain, i.e., the dynamic bead size. In a rough approximation, we can estimate $b \sim 2\pi/Q_x$.

Table 1 presents experimental data for Q_x, b, and l_K, as well as rotational energy barriers E^* for several polymers that we found in the literature. PDMS is the only polymer where the dynamic bead size has been estimated in Θ-solution and in the melt. Although the measurements were performed by different groups, the estimated values agree well (Table 1). This is expected for the Θ-solution and justifies our use of solution and melt data.

III. Discussion

III.1. Dynamic Bead Size. Figure 1 presents the estimated dynamic bead length b vs the Kuhn segment length, l_K. The dynamic bead size in all studied polymers, except PDMS and PEO, appears to be significantly larger than the Flory-style Kuhn segment length,[14] defined as $l_K = l_0 C_\infty/\alpha$ (α reflects a projection of the bond length on the backbone direction and is $\alpha \sim 0.83$ for PE[14]). Nevertheless, there is a clear correlation between b and l_K, at least, among the polymers with a carbon−carbon based backbone. It remains unclear why PDMS and PEO differ from all other polymers, although both polymers have backbone chemical structures different from the other polymers.

The difference between PDMS and polyisobutylene (PIB) has been emphasized earlier. These polymers have the same C_∞ and very close Kuhn segment lengths and are expected to have the same dynamic bead size.[15] Yet, the estimated value of b differs almost twice (Table 1, Figure 1). These results provide a clear illustration of the deficiency of the traditional assumption that the Kuhn segment presents the dynamics bead size. And it is apparently wrong for a θ-solution and for a polymer melt. It is known that siloxanes have very low energy barriers for intramolecular rotations.[25,26] The same is true for PEO. Richter and co-workers suggested that the larger dynamic bead size in PIB relative to PDMS can be connected to higher rigidity of the PIB chain. In their work, Richter et al.[15] employed the internal viscosity model of Allegra et al.[29,30] to evaluate how rotation barriers affect polymer dynamics. Using PDMS data as an input for PIB, Richter et al. were able to demonstrate that activation energy required to overcome internal viscosity effect is very close in its value to the rotation energy barrier of PIB. Thus, it was concluded that the mechanism responsible for the deviations of PIB from the Rouse dynamics is the internal viscosity effect governed by jumps across the rotational barriers. On the other hand, computer simulations performed by Krushev et al.[31] on polybutadiene (PB) showed that rotation energy barriers cannot be the only reason for deviations of chain dynamics from the Rouse model prediction. Comparing two models of PB chain, one chemically realistic chain and the other freely rotating version, Krushev et al. demonstrated that the shape of the scattering function stays identical for both models, although the dynamics for the freely rotating model of the PB chain exhibit much higher mobility. Krushev et al. suggested that an additional parameter must be responsible for the deviations of chain dynamics at smaller length scales from the Rouse model prediction. Thus, if one accepts the results of these simulations, the energy barriers are not the major reason for the observed large values of the dynamic bead size (Figure 1, Table 1). To analyze the role of the energy barriers in the dynamic bead size, we plot the ratio of b/l_K as a function of E^*/kT (where T is the temperature of the NSE experiments) in Figure 2.

Analysis of the data (Figure 2) indeed shows a trend for polymers with lower E^*/kT to have value of the bead size closer to the Kuhn segment length. It is, however, not a

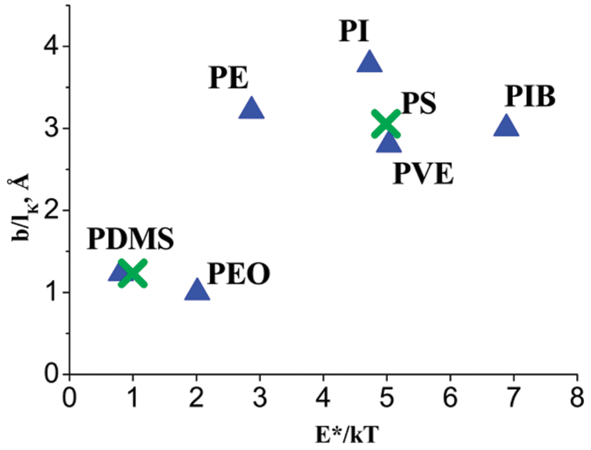

Figure 2. Ratio between dynamic bead size b and Kuhn segment length l_K in polymer melts (▲) and in Θ-solutions (×) versus the ratio E^*/kT at the temperatures of the neutron scattering experiments.

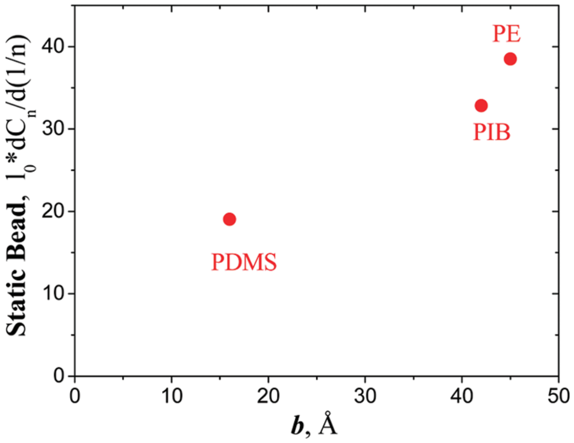

Figure 3. Static bead size from RIS calculations[38] versus the dynamic bead size obtained from neutron scattering data (Table 1). The values of l_0 used were 1.54 Å for PIB and PE and 1.64 Å for PDMS.

straightforward correlation and PDMS having significantly lower E^*/kT than PEO still exhibits larger b/l_K. Comparison of PEO, PE, and PIB also emphasizes the problem: (i) PE has E^*/kT ~50% higher than PEO, while the length of the dynamic bead differs by 4 times; (ii) while the bead size in PE and PIB is about the same, the value of E^*/kT in that case differs more than twice. It seems (Figure 2) that the ratio b/l_K depends more on the type of the backbone (C-based vs O-containing) than on the energy barrier. It is obvious that there should be additional mechanism responsible for the observed deviations from the Rouse-like behavior. In particular, Krushev et al.[31] suggested that the failure of the Rouse model might be caused by its inability to describe properly displacement of atoms on short length scales due to interchain interactions. In another words, effectively single-chain Rouse dynamic theory fails to capture the cooperative nature of the many-chains effect. It is known that segmental dynamics is highly cooperative in nature and involves many monomers from neighbor chains to move cooperatively on the length scale of a few nanometers.[32,33] The assumption that all these interchain interactions can be hidden in a simple friction coefficient is obviously an oversimplification.

We want to emphasize that significant difference between the Kuhn segment and the smallest dynamic bead size was noticed not only in neutron scattering studies. MD simulations performed by Paul et al.[17] showed that the dynamic structure factor $S(Q,t)$ in PE follows Rouse dynamics only up to $Q \sim 0.14$ Å^{-1}, in good agreement with the NSE data (Table 1). Although mechanical relaxation cannot measure the dynamic bead size directly, it can provide some indirect estimates. In particular, Lodge and co-workers[34] analyzed oscillatory flow birefringence in solution of PS with various molecular weights. This analysis reveals that the smallest dynamic bead size in PS has molecular weight ~5000. This is significantly larger than the expected Kuhn segment[13] (~720 g/mol) and agrees well with neutron scattering data from Higgins et al.[5] (Table 1). There is much other experimental evidence that the smallest dynamic bead size in PS (as one of the best studied model polymer) is significantly larger than traditionally defined Kuhn segment. In particular, this difference leads to deviations of the frequency dependence of mechanical moduli (G' and G'') from the expected Rouse behavior. Discussion of these examples is presented in the works by Ding et al.[35,36] Thus, not only neutron scattering and MD-simulation data but also some mechanical relaxation studies reveal significant discrepancies between the measured dynamic bead size (the smallest subchain where the Rouse dynamics is observed) and the traditionally defined Kuhn segment.

III.2. Static Bead Size. One of the traditional arguments in this discussion is that the Kuhn segment is defined from the static properties of the chain (eq 1). Thus the Kuhn segment presents a static bead size that might differ significantly from the dynamic bead size. The detailed static structure of polymers has not been extensively studied. However, Rawiso et al.[37] did exhausting analysis of PS structure using small angle neutron scattering with specific deuterations of monomers. Their analysis reveals that peculiarities of PS chemical structure affects the scattering function down to $Q \sim 0.03$ Å^{-1}. The authors concluded that “the popular assumption of approximating polystyrene by an infinitely thin thread is in error for a spatial scale corresponding to distances less than 50 Å”.[37] This length scale agrees surprisingly well with the estimate of the dynamic bead size in PS using neutron scattering[5] and oscillatory flow birefringence[34] measurements.

Another interesting example is analysis of chain dimension using rotation isomeric state (RIS) model.[38] The authors studied dependence of the chain dimension on polymerization ratio, in terms of C_n:

$$C_n = \langle R_{EE}^2 \rangle / n l_0^2 \tag{2}$$

in three polymers, PE, PIB, and PDMS. These polymers have similar C_∞'s and accordingly should have similar lengths of the Kuhn segment. The analysis reveals that C_n/C_∞ approaches its asymptotic value, $C_n/C_\infty = 1$, with different rates in these polymers. The slope of C_n/C_∞ vs $1/n$ in PIB is twice steeper than in PDMS, while PE has the slope slightly steeper than PIB.[38] This slope characterizes the rate with which the chain approaches the Gaussian behavior and depends on the length of the “effective random step” that is the static bead size. We want to emphasize that RIS calculations are based on equilibrium statistics of a single chain. So, they depend on energy minima of various conformational states (conformational rigidity), while energy barriers (dynamic flexibility) or intermolecular interactions do not play any role in this analysis. Yet it leads to the same conclusion: Even the static bead size is inconsistent with the traditional definition of the Kuhn segment. So, it is not just the problem of the Rouse model, it has deeper underlying physics.

It is interesting to note that the static bead size estimated from the RIS calculations for these polymers (the slope of C_n vs $1/n$ multiplied by the average bond length l_0) correlates to the dynamic bead size obtained from the neutron scattering

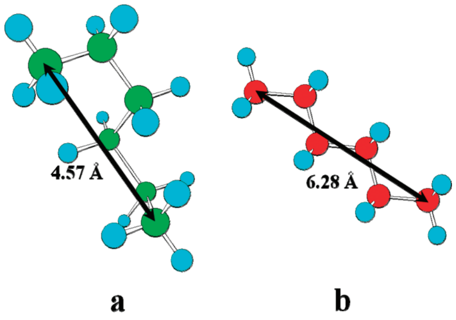

Figure 4. Illustration of the end-to-end distance for the same chain of three PE monomers (a) with trans and gauche conformations and (b) with all-trans conformations.

studies of the Rouse dynamics (Figure 3). This correlation suggests that although the static and dynamic bead size can be different, their lengths might be related. Moreover, RIS calculations are not affected by energy barriers; still the difference between PDMS and PIB is similar to the estimates of the dynamic bead size (Figure 2). This observation provides another argument that the energy barriers between intramolecular conformational states might be not the main reason for the difference in the bead size for polymers with similar C_∞'s. All these results emphasize a deficiency of the traditional definition of the Kuhn segment. It was stressed in ref 22 that C_∞ by definition is related to the size of the Gaussian coil. However, the bead size might depend on other chain parameters. So, the chains that have similar coil sizes at the same number of backbone atoms (e.g., PIB and PDMS) might have a significant difference in their bead sizes.

III.3. Deficiency of the Traditional Kuhn Segment Definition. The Kuhn length l_K can be introduced into the same eq 1:

$$\langle R_{EE}^2 \rangle = C_\infty n l_0^2 = N l_K^2 \tag{3}$$

In that case, however, we cannot disentangle the values of two variables, N and l_K, from a single equation. To introduce a second relationship, assumption of the equality of completely extended chains is usually involved:

$$L_{max} = \alpha n l_0 = N l_K \tag{4}$$

where $\alpha \sim 1$ reflects a projection of the bond length on the end-to-end vector of completely extended chain.[13] Assuming $\alpha = 1$ and combining eqs 3 and 4, one gets the traditional definition of the Kuhn segment length $l_K \approx C_\infty l_0$.

However, the assumption of the equal length (eq 4) is incorrect for most of polymers. It assumes that inside each bead the chain has extended conformation only. Let us consider a simple example of PE chain. In that case, eq 4 assumes that the chain should have all-trans conformations inside a single bead. However, the energy difference between trans and gauche conformations in PE is only ~2−4 kJ/mol.[39−44] It means that the probability of gauche conformation is about half of the probability of the trans conformation at $T \sim 500$ K (temperature of the NSE experiment). But PE has two gauche conformations and only one trans. Thus, the PE chain at this T would have an equal number of gauche and trans conformations. The schematic presented in Figure 4 illustrates that there will be a significant difference in the length of just three PE monomers depending on the conformational states. The difference will be much larger for chains containing more monomers. And it will depend not only on the total number of gauche and trans conformation but also on their sequence and direction of gauche conformations. This is a clear illustration that the assumption (eq 4) is incorrect for PE and for most of other polymers.

Because most of the real polymer chains will have various conformational states inside a single bead, one can only assume that $Nb < nl_0$. To overcome this problem, Ding et al.[35] introduced another parameter, the mass of the bead (random step) m_R. It defines the number of beads, $N = M/m_R$, where $M = nm_0$ is the molecular weight of the chain. In that case the bead size is defined by

$$b^2 = C_\infty \frac{m_R}{m_0} l_0^2 \tag{5}$$

However, it is not clear how to independently estimate m_R. Alternatively, the bead size can probably be defined through the parameter α (eq 4), which will reflect the averaged projection of a bond on the end-to-end vector of a single bead. This parameter will be significantly smaller than 1 for most of the polymers and probably can be estimated for each polymer using RIS calculations. In any case, one needs to introduce at least one more parameter (in addition to C_∞) to characterize the behavior of a real polymer chain.

Let us now discuss specifically the role of energy barriers (dynamic flexibility) and the energy difference (conformational rigidity) between various conformational states of the polymer backbone. Besides the results of simulations[31,38] that we already discussed, there are a few other results that question the role of energy barriers in the discrepancies between b and l_K. Figure 2 suggests that the chemical structure of the backbone (C-based vs O-containing) rather than energy barriers controls the ratio b/l_K. According to the definition (eq 4), the bead size can be equal to the Kuhn segment length only when the chain is fully extended inside each bead. This would be controlled by the population of different conformational states, not by the energy barriers. It is also important to note that the value of E^*/kT is rather small, it varies between 1 and 7 for presented here polymers (Table 1 and Figure 2). So low energy barriers cannot affect significantly the dynamics on time scale of chain modes. It is usually believed that the intrachain barriers affect segmental dynamics but become less important on the longer times of the chain modes. On the basis of these observations, we speculate that conformational rigidity is more important than dynamic flexibility (energy barriers) in defining the bead size. However, the height of the energy barriers might be related to the energy difference between the conformational states, and this could explain the trend observed in Figure 2.

IV. Conclusions

The presented analysis of neutron scattering data clearly demonstrate that the dynamic bead size (the smallest subchain that exhibits the Rouse-like dynamics) in most of the polymers is significantly larger than the traditionally defined Kuhn segment. Similar conclusions can be done from MD simulations and analysis of some mechanical relaxation data. Moreover, our analysis shows that even static bead size is inconsistent with the Kuhn segment length. We demonstrate the deficiency of the traditional definition of the Kuhn segment that is based on the assumption of the chain being completely extended (all trans conformation in the case of PE) inside a single bead. This generally would not be the case in real polymers. The presented analysis clearly demonstrates that presentation of a real chain by the bead-and-spring model, where all the chain chemistry can be hidden in a few parameters, requires more than just C_∞ to correctly describe the chain statistics and dynamic behavior. One needs at least one more parameter. We speculate that the reason for the observed discrepancies of the bead sizes and Kuhn segment length in polymers is most probably related to their conformational rigidity.

We also want to emphasize that the real length of the bead size is unimportant for long chains and most of the polymer applications. However, the nanometer-scale structures and their properties, whether in thin films or in some phase separated nanostructures, might be significantly influenced by the real size of the dynamic and static beads. At the length scale of the bead, $b \sim 2-5$ nm, the intramolecular forces change their behavior from entropic to energetic. And this change affects significantly the structure, its stability, and dynamic behavior.

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